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SUGGESTED PROCEDURE FOR THE CHEMICAL CHARACTERIZATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN HYDROCRACKED ATHABASCA BITUMEN

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INTRODUCTION

The polycyclic aromatic hydrocarbon (PAH) content in synthetic fuels influences their combustion characteristics. Some types of PAH are involved in reactor fouling during upgrading processes. Investigation of the chemical composition and homologue distribution changes of these PAH during processing is essential for tackling the problem of coke deposition on the reactor walls. The type distribution of the PAH in the processed products should be taken into consideration in choosing the reaction conditions.

Some PAH components could be considered as environmental hazards, because they are suspect carcinogens.

Environmental PAH samples are usually characterized by combined gas chromatography-mass spectrometric techniques (1). The heavy oils and bituminous products have highly complex chemical composition and thus require preliminary separation by use of both preparative liquid chromatography (LC) and high performance liquid chromatography (HPLC). The approach taken by our laboratory to characterize the PAH components in the synthetic products from bitumen involves the simultaneous use of various techniques. Chromatographic (LC, HPLC and GC) as well as spectrometric (MS, UV and spectrofluorometric) techniques are employed to acquire compositional and other quantitative information. This information is sought in terms of:

1. Ratios of the major PAH components.
2. PAH homologue distribution patterns.
3. Ratios of alkyl-substituted PAH components to bare ring types.
4. Presence of carcinogenic-suspect PAH components.

This report describes a suggested procedure for the separation and identification of the PAH components in the hydrocracked Athabasca bitumen product from the ERL hydrocracking process. The preliminary experimental details established during the attempt to choose an HPLC system that works for the bitumen products, are reported.

PRELIMINARY EXPERIMENTAL WORK

The hydrocracking conditions as well as the separation and identification scheme of the work are outlined in Figure 1.

Samples

(1) A polynuclear aromatic hydrocarbon concentrate eluted by benzene from a preparative liquid chromatographic column (dual-packed silica-alumina), according to a modification (5) of the API-USBM method.

(2) 140 pure PAH standard compounds (see Appendix), some containing S, N and O heteroatoms, were acquired and some of them used to determine retention data on both the HPLC and GC columns.

High Performance Liquid Chromatography (HPLC)

Selectivity of the following isocratic HPLC systems (columns and mobile phases) to the PAH pure compounds or PAH concentrates from hydrocracked Athabasca bitumen were checked:

(1) silica (particle size 5-10 microns) - Isooctane (3,3,5-trimethyl pentane)

(2) silica (particle size 5-10 microns) - n-Hexane

(3) Lichosorb-NH_2 (silica gel with bonded ammonia group) with n-Hexane as mobile phase (Bendix-Altex, 250 x 4.6 mm).

(4) Chromegabond-C_{18} (300 x 4.6 mm, ES Industries).
Mobile Phase: Acetonitrile-water mixture with composition ranging from 50 to 100% acetonitrile.

pump: Waters Associates Model 6000 (6000 p.s.i. max. pressure).

Flow rates: 2 ml/min with pressure drop of 1000 psi.

Injection: Valco valve with various loop sizes (7 µl, 25 µl, 100 µl and 250 µl) was used.

Detectors: (1) UV spectroflow monitor (Schoeffel SF 870).
(2) UV spectrofluorometer (Varian SF-330).
Cell volumes are 8 ml and 16 ml respectively.

Temperature Control: Water from a controlled temperature bath was circulated through the jacket of the column. Fixed temperatures (25°C) controlled to ± 0.1°C were used. A temperature gradient of 15 to 60°C was employed, and in this case the control was ± 0.2°C.

Sample Size: All the loop sizes were tried for sampling the bitumen PAH solution of 60 mg in 4 ml acetonitrile.

Fractions corresponding to HPLC separations were collected and introduced to GC and MS for further analysis and identification.

Gas Chromatography

The PAH samples of pure compounds diluted in benzene or PAH fractions from liquid chromatography were gas chromatographed under the following conditions:

Column:	3% OV-1, Chrom. W, a.w., DMCS, 80-100 mesh packed in 105 cm x 1.50 mm i.d. s.s. tubing.
Oven:	programmed from 75°C to 280°C at 4°C/min.
Carrier gas:	Helium at 45 cc/min.
Detector (FID) Temp.:	350°C
Injector Temp. :	275°C

A similar gas chromatographic system was also interfaced with the mass spectrometer.

Mass Spectrometry

A Finnigan Quadropole mass spectrometer-4000 was used in conjunction with a Nova-1 computer system.

RESULTS AND SUGGESTED PROCEDURE FOR FURTHER WORK

High Performance Liquid Chromatography Column - Mobile Phase System

Selectivity of the 4 used column systems was determined by a series of polynuclear aromatics containing 2 to 8 aromatic rings per molecule. Optimal selectivity was obtained on the Chromegabond-C_{18} system, with 80:20 acetonitrile-water as a mobile phase. At some lower acetonitrile concentrations selectivity was even more efficient on this column (better resolution of compound species), but retention was too high to allow complete elution of higher molecular weight polyaromatics. The efficiency of this column was 140-200 plates/cm.

The silica columns (Nos. 1, 2) were packed using ordinary chromatographic pump (6000 psi) and thus higher column efficiencies, usually attained by the use of slurry packers, were not possible. Selectivity on the Lichosorb-NH_2 column was low, and the retentions were too short to be of practical use in conjunction with the mass spectrometer.

The C_{18} column deteriorated after 4 months of continuous use with the standard polynuclear aromatic compounds and those derived from the hydrocracked bitumen. This was caused by irreversible sorption of the higher ring type compounds, especially those from the bitumen fractions. The use of a precolumn is suggested to alleviate this problem. The application of a solvent gradient system should also improve the separation as obtained under isocratic conditions.

Although the LC separation system silica-C_{18}/water-acetonitrile is so far, offering optimal possibilities for PAH characterization in bitumen samples (as confirmed by our experiments and published literature), yet it limits the characterization to those PAH that are soluble in acetonitrile. A variety of bonded chromatographic phase sorbents and mobile phases should be checked for their PAH selectivity.

The present LC sorbent-mobile phase systems resolve PAH on the basis of chemical affinity. Characterization of PAH's on geometrical basis, e.g. ring-type distribution, average diameter of ring systems or average molecular size could be more informative. Mobile phases that offer strong structure-temperature dependence (e.g. H_2O-soap mesophase) might be effective in separations based on the geometry of the ring systems.

The following experimental attempts are being performed:

- The temperature behaviour of water-potassium Laureate phase.
- Temperature dependence of PAH fluorescence spectra in H_2O-soap phases.
- Slurry packing of various columns.

Sample Size

Various combinations of sample concentrations and loop volume were tried. The appropriate sample concentration is sought for the following reasons:

(1) Reproducible retention data cannot be realized unless the retentions fall on the linear portion of the sorption isotherm.

(2) Concentration of the hydrocarbon material under the resolved liquid chromatographic peak should be sufficient to meet the mass spectrometric detection limits.

(3) The concentration should be within the linear response limits of the UV detector.

A loop size of 250 µl, and sample concentration of 60 mg/4 ml acetonitrile were satisfactory for fraction collection. The process was repeated 3-5 times to collect a sample that meets the above requirements.

Temperature Gradient

The elution sequences of some polynuclear aromatic hydrocarbons from the Chromegabond-C_{18} column with aqueous acetonitrile have been found to be influenced by temperature changes (2). The use of an efficient temperature gradient system would be useful to achieve complete elution of material by restraining resolution. A temperature range of 15 to 60°C was found suitable for this separation.

Collecting Cuts for GC and MS Analysis

The water has to be removed from the aqueous fractions collected from the HPLC columns before they are introduced to GC separations and mass spectrometric identification. The attempt to remove water by evaporation and nitrogen flushing caused excessive sample losses. It was possible to remove water by adding benzene to the aqueous acetonitrile cut. Two layers were formed, and the PAH were salted out by adding NaCl to the mixture. The organic phase was then separated and evaporated to 0.5 ml for further MS analysis.

Gas Chromatographic Analysis

The following eight pure PAH were used for calibrating the gas chromatographic column: phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, m-terphenyl, chrysene and perylene.

The resolution of the PAH bitumen fractions obtained from liquid chromatography was very poor on the OV-1 column due to the complexity of the samples. When a similar gas chromatographic system was interfaced with the mass spectrometer, considerable contamination from carboxylic acid esters was detected in the liquid chromatographic samples. Attempts are being made to eliminate this source of contamination.

From a literature search on the analysis of PAH it has been decided to use glass capillary chromatography as a means for separating the components under investigation. Two types of stationary phases will be employed in the study: OV-101 (6), and SE-52 (7,1). The studies of Grimmer (6), Giger (7) and Hites (1) will assist in establishing experimental conditions.

Mass Spectrometry

The work on the mass spectrometer resulted mainly in developing sample size to obtain peak concentrations that are identifiable within the sensitivity limits of the machine. Spectra were preliminarily characterized as to the number of aromatic rings in the separated PAH fractions.

Extensive library data search and MS scanning of pure compounds would be necessary for thorough identification of the PAH fractions. A computer search will be done for the major components (as expected from the HPLC and GC results) as well as the unknown compounds. The spectra will also be interpreted for homologue distribution patterns. Selective ion monitoring for certain polynuclear aromatics (carcinogenic suspects) is planned.

Spectrofluorometric Analysis

The spectrofluoremeter is the most specific LC detector. It has been used in this work in conjunction with the UV detector. It could be particularly useful for the identification of the PAH pure compounds that had undergone photomodification during storage.

Fluorescence spectra of the majority of PAH are not affected by alkyl substitution on the ring system (insignificant betachromic effect). Spectrofluorometry is the only method which could allow characterization of ring size distribution in the PAH samples (8). It is also the appropriate method for characterization and identification of the non-volatile materials in the bitumen which cannot be identified by GC-MS.

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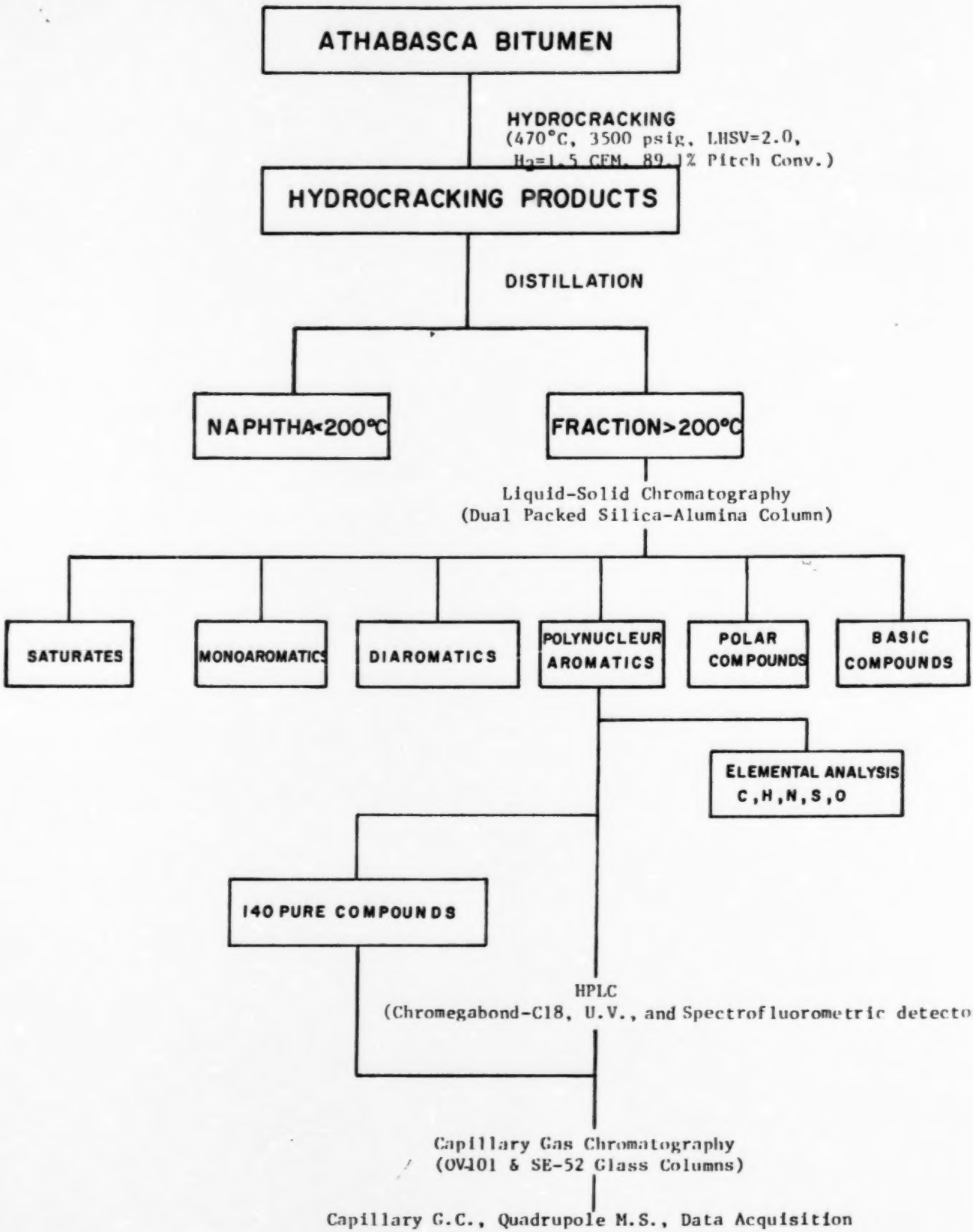

Separation and Identification Schematic of Polynuclear Aromatic Hydrocarbons in Hydrocracked Athabasca Bitumen

FIGURE 1

APPENDIX

List of

Polynuclear Aromatic Hydrocarbons
Acquired for the Research Project

Polynuclear Aromatic Hydrocarbons

2-Rings

Naphthalene

Biphenyl

Biphenylene

cis-stilbene (1,2-diphenylethene)

Indene

2-methyldiphenyl

3-methyldiphenyl

4-methyldiphenyl

4,4'-dimethyldiphenyl

1,4-dimethyl-5,6,7,8-tetrahydronaphthalene

1,3-dimethyl-5,6,7,8-tetrahydronaphthalene

acenaphthene

acenaphthylene

tetrahydroacenaphthene

1,2-dimethylnaphthalene

1,3-dimethylnaphthalene

1,4-dimethylnaphthalene

1,5-dimethylnaphthalene

1,6-dimethylnaphthalene

1,7-dimethylnaphthalene

2,3-dimethylnaphthalene

2,6-dimethylnaphthalene

2,7-dimethylnaphthalene

tetrahydronaphthalene

vinylnaphthalene

ethylnaphthalene

β-methylnaphthalene

2,3,5-trimethylnaphthalene

Azulene

4,6,8-trimethylzulene

Fluorene

3-methylindene

2-methylfluorene

phenylbenzoquinene

coumorin

dibenzo-p-dioxin

benzofuran

benzothiophene

phenylsulphide

benzylsulphide

benzylphenylsulphide

di-α-phenylethylsulphide

phenyl-γ-phenylpropylsulphide

phenyl-β-phenylethylsulphide

bis-β-phenylethylsulphide

phenyldisulphide

xanthene

xanthone (xanthene-9-one)

diphenylfuran

anthrone

acridine

2-methylacridine

carbazole

1-azacarbazole

3-Rings

fluoranthene

phenanthrene

anthracene

3-methylphenanthrene

2-methylanthracene

9-methylanthracene

9,10-dihydroanthracene

3,6-dimethylphenanthrene

o-terphenyl

m-terphenyl

p-terphenyl

4-benzyldiphenyl

1-phenylnaphthalene

2-phenylnaphthalene

α-benzylnaphthalene

1,2-benzofluorene

2,3-benzofluorene

3,4-benzofluorene

triptycene

tetradecahydrophenanthrene

1,2,3,4-tetrahydrofluoranthene

phenanthrenequinone

anthraquinone

1,2-benzodiphenylene sulphide

7,8-benzoflavone (α-naphthoflavone)

5,6-benzoquinoline

benzanthrone

phenanthridone

2-azafluoranthene

13-azafluoranthene

3,4-benzocridine

4-Rings

p-quaterphenyl

tetraphenylethylene

1,3,5-triphenylbenzene

2-phenylanthracene

9-phenylanthracene

1,1'dinaphthyl

2,2'-dinaphthyl

difluorenyl

triphenylene (9,10-benzophenanthrene)

tetracene (2,3-benzanthracene)

pyrene

1,2-benzanthracene

chrysene

5,12-dihydrotetracene

unsym-hexahydropyrene

1,2,6,7-tetrahydropyrene

1,2,3,6,7,8-hexahydropyrene

dodecahydrotriphenylene

octadecahydrochrysene

3-methylcholanthrene

22-methylcholanthrene

1-methylpyrene

3-methylpyrene

4-methylpyrene

9,10-dimethyl-1,2-benzoanthracene

3,4-benzofluoranthene

11,12-benzofluoranthene

α-truxene

ß-truxene

1,2,3,4-tetraphenyl-1,3-cyclopentadiene

1-azapyrene

benza[a]anthracene-7,12-dione

tetraphenylcyclopentadienone

bianthrone

5-Rings

perylene

picene

3,4-benzotetraphene

1,2,3,4-dibenzoanthracene

1,2,5,6-dibenzoanthracene

pentacene

3,4-benzpyrene (benzo[a]pyrene)

o-phenylenepyrene

rubicene

9,10-diphenylanthracene

6-Rings

1,2-benzpentacene

1,2,3,4-dibenzpyrene

5,10-dimethyl-3,4,8,9-dibenzpyrene

5-methyl-3,4,8,9-dibenzpyrene

anthanthrene

1,12-benzperylene

1,2,3,4-peri-dinaphthalenefluorene

1,12-phenyleneperylene

1,2,3,4-tetraphenylnaphthalene

anthanthrone

7-Rings

coronene

1,2,8,9-dibenzopentacene

decacyclene

8-Rings

rubrene (9,10,11,12-tetraphenylnaphthacene)

pyranthrene (1,2,7,8-dibenzoanthanthrene)